

Desorption of n -alkanes from graphene: a van der Waals density functional study

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A recent study of temperature programmed desorption (TPD) measurements of small n -alkanes (C_NH_{2N+2}) from C(0001) deposited on Pt(111) shows a linear relationship of the desorption energy with increasing n -alkane chain length. We here present a van der Waals density functional study of the desorption barrier energy of the ten smallest n -alkanes ($N = 1$ to 10) from graphene. We find linear scaling with N , including a nonzero intercept with the energy axis, i.e., an offset at the extrapolation to $N = 0$. This calculated offset is quantitatively similar to the results of the TPD measurements. From further calculations of the polyethylene polymer we offer a suggestion for the origin of the offset.

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I. INTRODUCTION

The increasing use of molecules on graphene and graphite surfaces for industrial applications calls for an improved atomic-scale understanding of the adsorption/desorption structure and process. The n -alkanes are linear chains of hydrocarbons, short versions of the polyethylene (PE) polymer. Using temperature-programmed desorption (TPD) Tait et al. (Ref. 1) measured the desorption energy and desorption rate preexponential factor of n -alkanes on graphene deposited on a Pt(111) substrate. The n -alkanes measured were short, with the number of C atoms $N \leq 10$. The desorption of n -alkanes from graphite surfaces was also measured by Paserba and Gellman [2–4], and from various other surfaces by a number of other groups [5], the surface materials including metals (Ag, Au, Cu, Pt, Ru), oxides (Al_2O_3 , MgO), and semiconductors (Si).

In most of the alkane desorption measurements the desorption energy was found to scale linearly with N for the short n -alkanes, but with a non-zero intercept with the axis of the desorption energy. The value found for this offset at $N = 0$ was sometimes found to be unphysically large, several times larger than the scaling coefficient. In another study Tait et al. [6, 7] analyzed their own data for n -alkane on MgO(100) desorption. They allowed the desorption prefactor to vary with chain length and found the desorption energy offset to be non-vanishing but small, of the size of or smaller than the scaling coefficient. When the same group of authors analyzed their data of n -alkanes on Pt(111) and on graphene (and also re-analyzed data from a number of studies by other groups for some of the above-mentioned surfaces) they found similar non-vanishing but small offsets for those desorption systems.

In this paper we use the first-principles van der Waals (vdW) density-functional method [8, 9], vdW-DF, to determine the n -alkane adsorption energy on graphene at

low coverages for short alkane chains ($N \leq 10$). This adsorption energy can be compared with the experimentally determined desorption barrier energy values. As in the experimental studies in Refs. 1, 6, and 7 we find a close-to-linear growth in adsorption energy E_a with chain length N , with a non-vanishing but small offset when extrapolated to $N = 0$

$$E_a = 7.23N + 6.44 \text{ [kJ/mol]}. \quad (1)$$

Here and below we use the term adsorption energy (E_a) for the energy found in our theory calculations. This corresponds to the desorption energy E_0 of isolated alkane molecules on graphene. By E_d we denote the experimental desorption energy, or desorption barrier, of an alkane molecule from partly covered graphene. In parts of the literature E_d is instead denoted $\Delta E_{\text{des}}^\ddagger$.

Contrary to analysis of the experiments, our calculations of the adsorption/desorption energy do not involve an assessment of the desorption prefactor. Our values of E_a are simply found from the differences in total energies of the system in the adsorbed and the desorbed states.

The outline of the paper is as follows. In Section II we describe the method of computation, including convergence tests of sensitive computational parameters. Section III presents our results and discussions, including a discussion of the definition of a monolayer (ML) of coverage of n -alkanes on graphene. Section IV contains our summary.

II. METHOD OF COMPUTATION

The n -alkanes are linear, saturated hydrocarbon chains absent of branches, with the general formula C_NH_{2N+2} , $N > 0$. Very long such chains (in principle infinitely long) are known as the PE polymer. In this paper we analyze the adsorption on graphene of the ten smallest n -alkanes ($1 \leq N \leq 10$), of H_2 , and of PE, all in the stretched form, which is the trans conformation.

Our interest in the alkane desorption was sparked by the TPD experiments of Tait et al. [1] and their analysis leading to the experimentally determined desorption

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energy. We determine the adsorption energy by use of first-principles density functional theory (DFT), employing the method vdW-DF [8, 9] as detailed in several other publications [10–12] but here with the vdW interaction treated fully selfconsistently [9]. We calculate the total energies of the adsorption system using the DFT program GPAW [14] with vdW-DF [8, 9] in a Fast-Fourier-implementation [15].

Figure 1 illustrates the adsorbed *n*-pentane molecule on graphene, and the unit cell used in our calculations for $N = 5$. The lateral sizes of all the unit cells used are listed in Table I.

For each of the adsorbed alkane molecules we determine the optimal positions of the atoms by minimizing the Hellmann-Feynman forces. These are derived from gradients in the self-consistently determined electron density. This optimization also adjusts the intramolecular bond lengths to the most favorable value in the adsorption state. After this optimization we obtain the total energy of the adsorbate-graphene system, $E_{\text{near}}^{\text{vdW-DF}}$.

The GPAW code is an all-electron DFT code based on projector augmented waves [21] (PAW) and using finite differences. In several of our previous vdW-DF applications we used self-consistent calculations with the generalized gradient approximation (GGA) to determine the electron density and part of the total energy, followed by non-selfconsistent calculations to determine the total energy within vdW-DF. This allowed us to focus on either the GGA need for accuracy in choice of computational parameters and methods (for example the need of a fixed amount of vacuum in the total system [22–24]) or the vdW-DF need for accuracy in other parameters and methods (for example the need for fixating the local electron density grid [11, 25, 26]). When carrying out selfconsistent calculations for vdW-DF all of these requirements must be met in all calculations. Below the most important of these choices are described.

We model the adsorption system by means of an orthorhombic unit cell, periodically repeated in all directions. The unit cell contains sufficient space in the plane of graphene for the repeated images of the *n*-alkane molecules to interact only little. As explained below, we make sure to explicitly subtract the small lateral interaction of the periodic images of the molecules from our results [12, 27]. In the direction perpendicular to graphene the introduction of ~ 19 Å of vacuum above the adsorbed alkane ensures that no interaction across unit cell boundaries takes place.

For the smallest of the alkanes, methane ($N = 1$), we use a unit cell of size $3\sqrt{3}a_g \times 3a_g \times 23.0$ Å and for the largest alkane considered here, *n*-decane ($N = 10$), we use a $5\sqrt{3}a_g \times 4a_g \times 23.0$ Å unit cell. Here $a_g = \sqrt{3}a_0$, with $a_0 = 1.43$ Å, is the clean graphene lattice constant as found in our calculations by relaxing the lateral size of the unit cell. The unit cell sizes used for the other calculations ($N = 2, \dots, 9$) are listed in Table I.

We choose the real-space grid for representing the

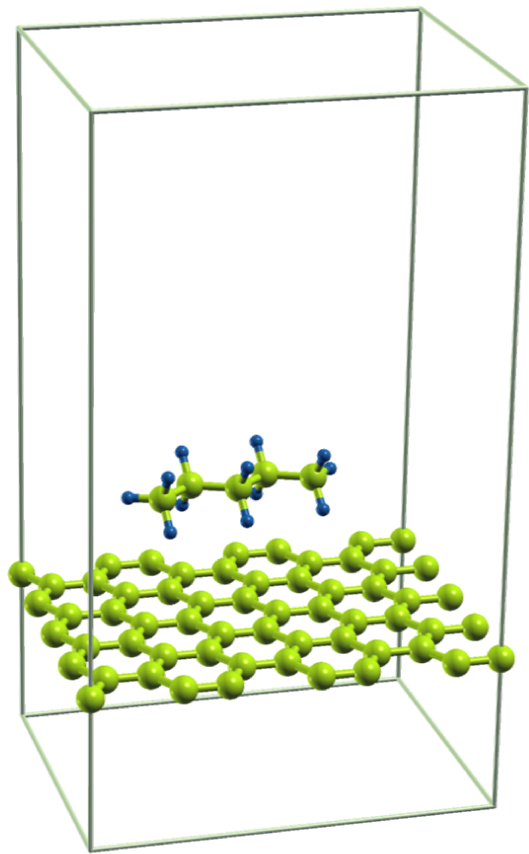


FIG. 1: Illustration of *n*-pentane ($N = 5$) adsorbed on graphene. One unit cell is shown including a repetition of the graphene carbon atoms that are positioned on the unit cell boundary. C atoms are represented by large spheres and H atoms by small spheres. Figure created using XCrySDen [16].

wavefunctions in the PAW procedure to have a distance less than 0.11 Å between nearest-neighbor (nn) grid points. The (valence) electron density is represented on the same grid with additional grid points at half the nn distance, values obtained from interpolation of the electron density and addition of compensation charges. The choice of these relatively dense (wavefunction and electron density) grids is important for the quality of the evaluation of the nonlocal correlation contribution [25].

The Brillouin zone of the unit cell is sampled according to the Monkhorst-Pack scheme by means of a $2 \times 2 \times 1$ k -point sampling. Increasing the k -point sampling to $4 \times 4 \times 1$ changes E_a less than 0.7 meV per molecule (0.07 kJ/mol). We further make sure that the calculation is accurately converged with respect to total energies. We impose a convergence threshold such that the total energy changes less than 0.1 meV per unit cell, or less than approximately 10^{-6} eV per atom in the unit cell, in the last three iterations. This convergence threshold is several orders of magnitude smaller than the default settings of GPAW.

TABLE I: Adsorption (desorption) energies from theory (E_a) and experiment (E_d and E_0), center-of-mass distance from graphene d_{cm} , area A of one alkane molecule in a full monolayer, unit cell used in calculations, and corresponding estimated coverages θ , for the small n -alkanes (C_NH_{2N+2} , $N = 1 - 10$). In our calculations we use orthogonal unit cells and a graphite lattice vector $a_g = \sqrt{3}a_0$ with $a_0 = 1.43$ Å. The experimental values of E_0 — corresponding to the limit of 0 ML coverage and no defect sites — is found from Eq. (5) with the use of parameters given in Table IV of Ref. 1. The coverage for PE is found from an estimate of the PE-PE interaction distance in the PE crystal, as described in the text.

		This work					Experiments		
		N	Unitcell	θ	d_{cm}	E_a	A	$E_d(0.5 \text{ ML})$	E_0
				[ML]	[Å]	[kJ/mol]	[Å ²]	[kJ/mol]	[kJ/mol]
H ₂	0	$2\sqrt{3} \times 3$			3.39	6.8	0.070		
methane	1	$3\sqrt{3} \times 3$	0.16	3.64	14.6	0.152	15 ^a	14.1	13.6
ethane	2	$3\sqrt{3} \times 3$	0.22	3.80	20.9	0.216	20.9 ^b	24.6	23.8
propane	3	$3\sqrt{3} \times 3$	0.28	3.90	27.7	0.288	27 ^a	32.1	30.6
n -butane	4	$3\sqrt{3} \times 4$	0.26	3.97	34.6	0.358	32.7 ^c	40.8	38.9
n -pentane	5	$3\sqrt{3} \times 4$	0.31	3.86	42.8	0.443	39 ^a		
n -hexane	6	$4\sqrt{3} \times 4$	0.26	3.96	49.6	0.514	45.6 ^d , 44.8 ^e	63.0	60.3
n -heptane	7	$4\sqrt{3} \times 4$	0.30	3.90	57.7	0.598	51.6 ^f		
n -octane	8	$5\sqrt{3} \times 4$	0.27	3.89	65.5	0.679	57.2 ^f , 57.7 ^d , 56.2 ^e	72.6	71.0
n -nonane	9	$5\sqrt{3} \times 4$	0.30	3.87	73.0	0.757	63.5 ^f		
n -decane	10	$5\sqrt{3} \times 4$	0.32	3.86	80.3	0.832	69.0 ^f , 69.7 ^d , 68.9 ^e	91.4	84.5
polyethylene (1)		$5\sqrt{3} \times 1$	0.21	3.83	7.2 ^g	0.074 ^g			

^aLinear interpolation of the experimental data available for other values of N , $A(N) \approx 9 + 6N$ Å².

^bNeutron diffraction data at submonolayer coverage, Ref. 17.

^cNeutron diffraction data at 11 K, Ref. 18.

^dX-ray diffraction data at submonolayer coverage, Ref. 19.

^eNeutron diffraction data at submonolayer coverage, Ref. 19.

^fX-ray diffraction data, Ref. 20.

^g E_a per C atom in PE. Each unit cell has two units of CH₂.

We determine the adsorption energy E_a as the difference in total energy between a system with an alkane adsorbed in the optimal geometry and a system with the alkane moved far away from graphene. It is well known that in the vacuum region of the system small spurious exchange energy contributions add to the total-energy [22–24]. To cancel these contributions we use the same unit cell for the calculation of the adsorbed state and for the desorbed state. We make sure that the height of the unit cell allows the fragments (graphene and alkane molecule) to be far apart within the unit cell. With unit cell height 23 Å the maximum possible separation is ~ 11 Å, sufficient for the alkane to count as desorbed.

The correlation energy E_c in the total energy for the vdW-DF functional is split [28] into a nearly-local part E_c^0 and a part that includes the most nonlocal interactions E_c^{nl} ,

$$E_c = E_c^0 + E_c^{\text{nl}}. \quad (2)$$

In a homogeneous system the term E_c^0 is the correlation E_c^{LDA} obtained from the local density approximation (LDA), and in general [8] we approximate E_c^0 by E_c^{LDA} . The term E_c^{nl} vanishes for a homogeneous system. It describes the dispersion interaction. The form of E_c^{nl} is

derived in Ref. 8. It is a truly nonlocal functional

$$E_c^{\text{nl}}[n] = \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' n(\mathbf{r}) \phi(\mathbf{r}, \mathbf{r}') n(\mathbf{r}') \quad (3)$$

given by a kernel ϕ which is explicitly stated in Ref. 8.

E_c^{nl} exhibits a small sensitivity to changes in the local real space grid, for example translations of the nuclei positions by a non-integer number of real-space grid points [11, 25, 26]. The procedure to ensure high-quality results that include contributions from changes in the intra-molecular bonds is described in more detail in Refs. 13 and 29, and is reviewed here.

We derive the adsorption energy in three steps. First we carry out a vdW-DF calculation of the adsorbed molecule, yielding the total energy $E_{\text{near}}^{\text{vdW-DF}}$. Next we carry out a vdW-DF calculation of the molecule moved off graphene rigidly, which gives us the total energy $E_{\text{far}}^{\text{vdW-DF}}$. Finally, we let the molecule relax into the gas phase structure. From the last step we obtain values of the total energy in the first (deformed for adsorption) and in the last (gas phase) situation, $E_{\text{deform}}^{\text{PBE}}$ and $E_{\text{gas}}^{\text{PBE}}$ respectively. In this last relaxation study step we use the Perdew-Burke-Ernzerhof [30] (PBE) variant of GGA. The adsorption energy E_a , shown in Table I, is

then found from

$$-E_a = E_{\text{near}}^{\text{vdW-DF}} - E_{\text{far}}^{\text{vdW-DF}} + E_{\text{deform}}^{\text{PBE}} - E_{\text{gas}}^{\text{PBE}}. \quad (4)$$

For the calculation of $E_{\text{near}}^{\text{vdW-DF}}$ we determine the optimal position of the alkane molecule adsorbed on graphene. The Hellmann-Feynman forces on the alkane atoms are minimized. All graphene atoms are fixed in space in this and all other calculations.

For the calculation of $E_{\text{far}}^{\text{vdW-DF}}$, we move the alkane molecule (rigidly) off of the graphene sheet by translating the molecule by 75 grid points, corresponding to adding ~ 8.13 Å to the graphene-alkane distance. This yields an alkane-graphene separation of approximately 11-12 Å both between fragments within the unit cell and fragments in the vertically repeated images. By translating the alkane an integer number of grid points the nuclei locally maintain the same positions with respect to the grid, thus avoiding any possible effects of describing the electron density differently on a shifted grid [25, 26]. This intermediate reference energy $E_{\text{far}}^{\text{vdW-DF}}$ is then subtracted from $E_{\text{near}}^{\text{vdW-DF}}$. We use the same unit cell size, number of real space grid points, and number of k -points as for the adsorption calculation.

The use of an intermediate reference energy subtracts not only intra-molecular contributions (the alkane molecule is identical in the two calculations) but also any direct alkane-alkane interaction across unit cell boundaries. This is usually a small contribution in our calculations.

The last set of calculations finds the energy gain $E_{\text{deform}}^{\text{PBE}} - E_{\text{gas}}^{\text{PBE}}$ of relaxing the isolated alkane molecule from the slightly deformed structure of the adsorbed state. This energy gain is not expected to have any long-range component. The E_c^{nl} term of vdW-DF depends slightly on the density grid points positions with respect to the molecule, and we therefore, as a matter of principle, choose to perform this part of the calculation using instead the GGA variant PBE [30].

It should be noted, though, that in this study it does not numerically matter to the energetics whether we use PBE or vdW-DF in this last relaxation-study step.

III. RESULTS AND DISCUSSION

The alkane molecules deform very little upon adsorption, compared to their gas phase structure. In the gas phase, calculated with vdW-DF, we find for n -pentane the average C-C bond length 1.541 Å. The C-C distance varies slightly along the carbon chain, with the smallest values towards the ends and the largest values around the center of the chain, but the difference only amounts to 0.001 Å. For n -nonane the C-C bond lengths along the chain differ by 0.002 Å, again with the largest values around the center of the chain. We find similar bond lengths and bond length variations for the other alkanes.

Values of the average C-C bond length found by experiment [31] for n -alkanes with $N = 2$ to 7 are in the

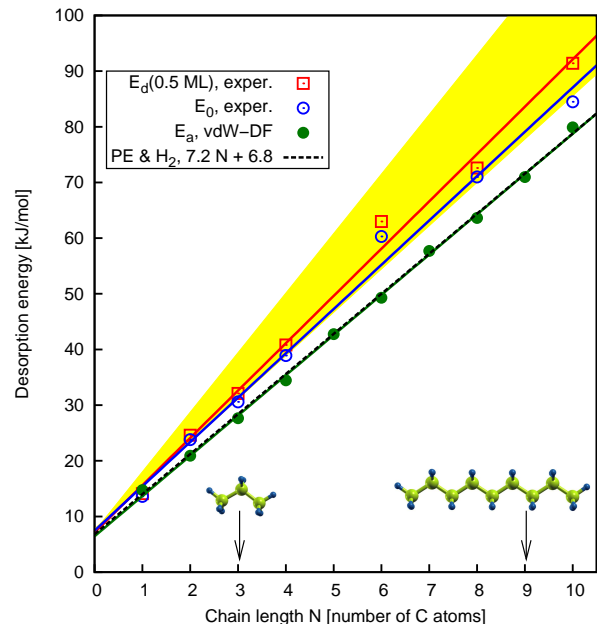


FIG. 2: Desorption energy as a function of the length of the n -alkane chain. Solid points are our results, open points are from the TPD measurements by Tait et al. [1]. Linear regression lines for the three sets of data points are also shown, including the extrapolations to $N = 0$. The dashed line has the slope from our calculations of the adsorption of PE, with the H_2 adsorption energy added to represent the ends of the alkanes. The shaded area encompasses the estimated (by Ref. 1) errorbars of the 0.5 ML experimental data.

range 1.526 Å (n -propane) to 1.536 Å (ethane). Our results for the bond lengths thus deviate less than 1% from experiment.¹

When an alkane molecule is adsorbed on graphene we find that the bond lengths are only slightly affected. For pentane the adsorbed molecule (Fig. 1) has an average C-C bond length 1.543 Å, a change from the gas phase by 0.002 Å (or 0.1%), and the bond lengths are still larger towards the middle of the chain (1.544 Å) compared to the bonds at the ends of the chain (1.542 Å). For the other alkanes we find the average C-C bond length in the range 1.540 Å (ethane) to 1.544 Å (octane and nonane), and for all alkanes the bonds towards the middle of the chains are longer than those at the ends.

Thus, structural changes caused by the adsorption are very small. Energetically, the changes are also very small: using PBE for the reasons stated in the previous section we find the difference in total energy $E_{\text{deform}}^{\text{PBE}} - E_{\text{gas}}^{\text{PBE}}$

¹ When comparing the values of the bond lengths with experiment it should be kept in mind that many exchange-correlation approximations, like the vdW-DF and also many of the GGA approximations, find covalent bond lengths that can deviate up to a few percent from the experimental values.

approximately 2 meV (0.2 kJ/mol) per C-C bond for all the alkanes studied here.

All calculations of the adsorbed alkanes presented above are for an orientation with the alkane carbon skeleton parallel to graphene. We started out the process of optimizing the atomic positions with the carbon skeleton parallel to graphene, and all calculations reached an energetic minimum when parallel to graphene. To check if this is also the global minimum we further calculated the total energy for alkane molecules that initially were oriented with their carbon skeleton perpendicular to graphene, i.e., rotated 90° around their axis. For these, we also find a local minimum, but with a total energy larger (less favorable) than for the configuration with the backbone parallel to graphene. For example for pentane we find that the loss of total energy going from the perpendicular orientation to the parallel orientation is 48 meV (4.6 kJ/mol).

Table I lists the adsorption (desorption) energies obtained from theory by us and through TPD measurements by Tait et al. [1]. As shown in Figure 2 the calculated adsorption energy values grow linearly with the size of the alkane molecule, N , with an off-set comparable to that from experiments. Although the coverage of adsorbed alkanes in our calculation is 0.2–0.3 ML (with full coverage defined as described further below) the subtraction procedure involving the two first terms in (4) ensures that all direct alkane-alkane interactions are eliminated. Thus our results should be compared with experimental results for single alkane molecules desorbed from otherwise clean and defectless graphene (coverage 0 ML), E_0 .

In Ref. 1, the model used for describing the desorption energy E_d as a function of the coverage θ and the number of alkane carbon atoms N is

$$E_d(\theta, N) = E_0(N) + \gamma(N)\theta + E_{\text{def}}(N)\exp\left(-\frac{\theta}{\theta_{\text{def}}(N)}\right). \quad (5)$$

The $E_0(N)$ is the contribution from a defectless surface (here: graphene) in the absence of adsorbate-adsorbate interactions. The term $\gamma(N)\theta$ accounts for the increase in desorption energy due to the interaction with other adsorbates on the surface, and the third term describes the effect of defects in the surface. The model is introduced in Ref. 6 for n -butane on MgO(100). For general (small) n -alkanes on graphite the parameters γ , E_{def} , and θ_{def} are given in Table IV of Ref. 1. In our calculations graphene is defectless and there are no lateral interactions between molecules. Therefore our adsorption energies E_a should be compared with the experimental quantity E_0 , listed in Table I.

In Figure 2 are shown the experimental results E_d at $\theta = 0.5$ ML, with error estimates within the shaded area (from Table III of Ref. 1), and E_0 at zero coverage, together with our adsorption energies E_a . Comparing E_a with E_0 we find that our theory adsorption energies deviate somewhat from the experimental results, with values from theory about 10% smaller than E_0 . Hexane is an exception: our vdW-DF value E_a is 18% smaller than

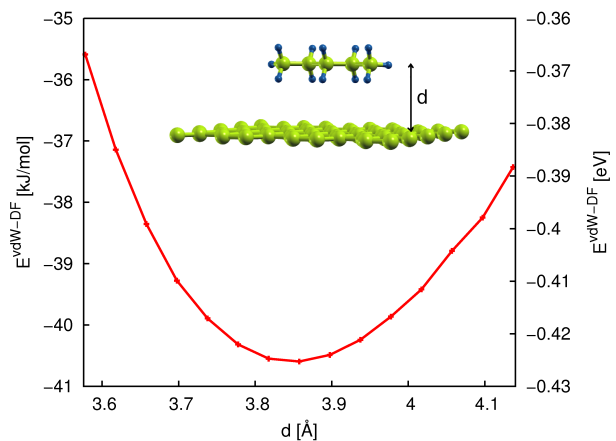


FIG. 3: Potential energy for n -pentane on graphene. The potential is calculated like $-E_a$ in (4) but with the center of mass of pentane fixed at the distances d from graphene. The minimum of the curve corresponds to the adsorption energy E_a and distance d_{cm} .

E_0 . However, for hexane the experiment deviates from the linear growth with N whereas our theory result does not.

The solid linear curves in Figure 2 are the linear regression curves for E_d , E_0 , and E_a . The experimental curves are described by $E_d = 8.50N + 7.11$ (Ref. 1) and $E_0 = 7.96N + 7.46$, and we find for the theory results the relationship $E_a = 7.23N + 6.44$, all given in units of kJ/mol.

The shaded area in Figure 2 shows the estimated errors in the values of E_d as provided by Ref. 1; it is reasonable to expect similar error estimates on the experimental E_0 values but these are not available to us.

In Figure 3 we show the potential energy curve for n -pentane as pentane is moved away from graphene, obtained with the vdW-DF functional. The points of the curve are obtained as described by (4), with three sets of calculations, however with the center of mass of the molecule kept fixed at the distance d above graphene. All internal atomic positions of pentane are allowed to relax.

Figure 3 shows that the potential is shallow around the adsorption position. For example, moving the center of mass of pentane 0.1 Å towards or away from graphene results in an energy increase of only about 1 kJ/mol, or 10 meV. For our calculations we also report in Table I the distance d_{cm} between the center of mass of the molecule and the graphene sheet at the adsorption distance, which ranges from 3.64 Å (methane) to 3.96 Å (hexane). Because of the shallow minimum there is some uncertainty in determining d_{cm} .

Although we subtract the direct alkane-alkane interactions from the adsorption energy it is in principle possible that small indirect alkane-alkane interactions remain if the molecules are placed too close, e.g., closer than in

a monolayer coverage. Such indirect interactions would affect the atomic positions of alkane from nearby alkanes. We must therefore make sure that the alkanes are sufficiently far apart that such indirect interactions are negligible. To quantify this, we determined the coverage of alkanes in our calculations in units of ML, for each of the alkanes as well as for H₂ and PE.

We describe the coverage of molecules on graphene by fractions θ of a molecular ML. One ML is a one-molecule thick coating of a surface, as found by experiments. In order to find θ for our calculations we need to know for a full ML how many molecules cover a specified area of graphene, or how large an area A does one molecule cover, in average. Couto et al. [32] found by means of STM that for various n -alkanes adsorbed on graphite the coating layer is highly ordered. The ordering at such high coverage is affected both by the adsorbate-adsorbate and the adsorbate-substrate interactions. Disordered arrangement is only activated above a critical temperature. For most of the molecules we find the definition of 1 ML from experiments reported in the literature [17–20], but for methane, propane, and pentane we use an estimate based on a linear interpolation of the experimental data available for other values of N , $A(N) \approx 9 + 6N \text{ \AA}^2$. From the values of $A(N)$ and the sizes of our unit cells we calculate the coverages $\theta(N)$ used in our calculations.

For PE we estimate θ from the PE-PE interaction distance in the PE crystal. In an earlier study [33] one of us identified the optimal PE crystal structure within a vdW-DF characterization. From that study we estimate the optimal centerline-to-centerline distance between the polymers to be 4.5 Å. The separation of the PE polymers used in the present study is $5\sqrt{3}a_g \approx 21 \text{ \AA}$. This gives a coverage for PE $\theta_{\text{PE}} \approx 4.5 \text{ \AA}/21 \text{ \AA} \approx 0.21$.

As summarized in Table I, the coverages used in our study are always less than a third of a ML, with values $\theta = 0.16 - 0.32$, sufficiently sparse for indirect interaction effects to be neglected.

Almost all the available experimental results on alkane desorption from various surfaces derive from TPD measurements measuring the desorption rate r . In order to extract the desorption energy from r the preexponential desorption rate ν was earlier often assumed to have the value 10^{13} s^{-1} . This value is accepted as a reasonable value for first-order processes in surface physics of atoms and is derived from traditional transition state theory. However, the more complex processes of molecular desorption are not necessarily as well described by that particular value, nor more generally by a value that is constant for all n -alkanes.

The desorption rate r may be described by the Polanyi-Wigner equation

$$r(\theta, T) = -\frac{d\theta}{dt}(\theta, T) = \nu(\theta, T)\theta^n e^{-E_d(\theta)/k_B T} \quad (6)$$

for n th order desorption, here $n = 1$. Assuming a constant value of ν for the small ($N < 12$) n -alkanes the TPD desorption rates give linear growth in E_d with num-

ber of alkane segments N but with a very large offset [5] at $N = 0$. The offset is much larger than the segmental increment in E_d . Lei et al. speculated [34], and Tait et al. showed from analysis of TPD experiments [1, 7], that ν takes other and varying values in alkane desorption. This was shown for various surfaces like graphite, Pt(111) and MgO(100). By treating ν as a fitting parameter along with E_d , modified and varying values of ν are found. Such analysis leads to a more modest value of the offset of E_d at $N = 0$, at the size of or smaller than the segmental increment in E_d [1, 7].

In particular, it was found [1] that on graphite ν varies from $10^{13.0} \text{ s}^{-1}$ for methane to $10^{17.8} \text{ s}^{-1}$ for n -decane. Thus the small molecules have a desorption prefactor similar to that from theory for atoms, whereas the prefactors for the larger molecules deviate strongly from this. Taking these variations into account the desorption energy offset at $N = 0$ is reduced to 7.11 kJ/mol, with a segmental increment in E_d of 8.50 kJ/mol. Similar results were obtained for small- N n -alkane desorption from Pt(111) and MgO(100).

It thus seems that the previously published large values of the $N = 0$ offsets can mostly be explained [1, 6, 7] as an effect of not allowing ν to vary for the small n -alkanes. Nevertheless, an offset of a smaller size does remain even in the re-analyzed data.

In the literature the origin of the offset has been debated [1, 5, 34]. Even though the values of the offsets may be reduced as discussed above, also the remaining offset begs an explanation. Lei et al. summarize the discussions by listing a number of suggested reasons: (i) the different binding to the surface of the methyl end groups ($-\text{CH}_3$) compared to the methylene segments ($-\text{CH}_2-$); (ii) the effect from the chain length dependence on the polarizability of the alkanes; (iii) the effect of needing different temperatures for the various alkanes for measuring r ; (iv) possibly the desorption process cannot be described as a first-order process, e.g., if the alkanes adsorb in islands or other structures; (v) possible lattice mismatch of the alkanes with the surface; and finally (vi) chain length dependence of ν . The latter suggestion reduces the offset to a more modest value, as discussed above.

Without going into details of all of the above-mentioned suggestions we note that our calculations are in a sense more direct than the desorption energies derived from the TPD measurements. In our calculations the preexponential factor ν is not involved, temperature variation is not an issue, and we do not let the alkanes adsorb in islands. Our results are in agreement with the results presented in Ref. 1 where the approach of a variable desorption prefactor was used. In particular, our theoretically calculated value of the offset agrees very well with that obtained by Tait et al. Here we present a simple model study to discuss the suggestion (i) of end-group effects.

Our calculated adsorption energy for PE corresponds very well with our similarly calculated adsorption energy per segment of the alkanes (when neglecting the offset).

PE is similar to the alkanes, but it does not (at least not ideally) include methyl end groups. In our calculations we describe PE adsorbed on graphene by periodically repeating two CH_2 units, thus explicitly avoiding end groups. We find (Table I) the adsorption energy per methylene unit in PE, 7.2 kJ/mol, which corresponds very well to the energy 7.4 kJ/mol we find per (methylene or methyl) unit for small n -alkanes.

It is natural to expect that the two extra H atoms attached to the ends of the alkane molecules (in the methyl groups) also contribute to the adhesion, thus affecting the offset in the adsorption energy. We present a calculation of a H_2 molecule adsorbed on graphene to test a hypothesis of simple additivity of N methylene segments ($-\text{CH}_2-$) and two additional H atoms. This is thus an even simpler model for n -alkane than adding methyl to the ends of a string of methylene segments.

Our calculation of H_2 on graphene yields the adsorption energy 6.8 kJ/mol. In the calculated curve for E_a the offset is 6.44 kJ/mol. Our results for PE and H_2 fit nicely to this simple additivity model. The curve with slope derived from PE adsorption and offset derived from H_2 adsorption is plotted in Figure 2 (dashed line).

Arguments raised against the end-group explanation have been that experiments [34] for cyclic alkanes on Cu(111) and Pt(111) also show an offset for extrapolation to N even though the cyclic alkanes do not have any end groups. However, those results were extracted using fixed values of ν and yield large offsets (36 kJ/mol for Pt, 19 kJ/mol for Cu) both for the cyclic alkanes and their linear equivalents. In that analysis the effect directly on the desorption barrier from the end groups is estimated to 2 kJ/mol per linear alkane for both Pt and Cu surfaces. We cannot judge whether the value of the cyclic-to-linear difference in desorption barriers [34], 2 kJ/mol, would remain after a re-analysis of the desorption energies with more variation of ν , along the lines of those of Tait et al.

IV. SUMMARY

We present a computational study of the adsorption of small n -alkanes on graphene using the van der Waals density functional method vdW-DF. Recent desorption experiments [1] have shown desorption barriers growing linearly with the size of the alkane molecule, but with an offset in the limit of zero length. Here we reproduce in our calculations the linear dependence on the alkane length including an offset the same size as obtained by the experiments. With the help of our calculated adsorption energy of polyethylene and H_2 molecules we argue that a simple additivity assumption of alkane methylene ($-\text{CH}_2-$) units plus two extra H atoms for the alkane ends explains the size and origin of the energy offset very well. Summing up, our calculations thus give support to the suggestion that the offset measured in n -alkane desorption experiments (after correction for effects of varying ν) can be explained by the n -alkane end groups being different from the methylene segments of the n -alkanes.

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